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Development of a Simple Indicator for Measuring the
Performance of Incinerators, Industrial Furnaces, and
Boilers Burning Hazardous Waste

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Development of a Simple Indicator for Measuring the Performance of
Incinerators, Industrial Furnaces, and Boilers Burning Hazardous Waste

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Abstract

Current regulations in the Resource Conservation and Recovery Act (RCRA) use Destruction and Removal Efficiency (DRE) of the Principal Organic Hazardous Constituents (POHCs) in the feed as the main regulatory parameter to determine performance of facilities incinerating hazardous waste during a RCRA trial burn. The calculation of DRE, however, is expensive and time consuming to perform on a regular basis, and it is impossible to measure DRE continuously using existing on-line analyzers. In addition, DRE does not address the issue of potential emissions of toxic compounds that can be formed as products of incomplete combustion (PICs) during the incineration process.

Experiments on a 73 kW (250,000 Btu/hr) rotary kiln incinerator simulator equipped with a 58.4 kW (200,000 Btu/hr) afterburner/control temperature tower have been performed to aid in the development of a uniform, easy-to-measure performance indicator for comparison of transient puffs generated by batch incineration of different types of surrogate wastes. By utilizing time-integrated responses from process gas analyzers, rather than instantaneous or averaged responses, it is possible to derive an indicator of the relative degree of local oxygen starvation that waste material was exposed to while passing through the incinerator. This indicator, the Unsatisfied Oxygen Demand (UOD), is a quantity that reflects the fate of all carbonaceous material initially in the feed. UOD takes into account emissions of CO, hydrocarbons, and soot, weights them according to their stoichiometric oxygen requirements, and compares these parameters to the stoichiometric requirements of the initial waste. An advantage of UOD as an indicator of incinerator performance is that it takes into account the variations in PIC speciation that result from different waste compounds. Although the research to derive an acceptable value for UOD is still in its infancy, the concept shows promise as a "back of the envelope" calculation that can be done semi-continuously without the need for sophisticated, expensive chemical analyses.

Introduction

Incineration is combustion. However, measurement of incinerator performance is complicated by several factors, including non-homogeneities in the waste feed, and the complex mixtures produced during periods of suboptimal combustion of the waste. Current regulations in the Resource Conservation and Recovery Act (RCRA) require a trial burn prior to an incineration facility's being granted a permit to burn hazardous waste. The trial burn is meant to certify that each Principal Organic Hazardous Constituent (POHC) contained in the waste at greater than 100 ppm by weight is properly destroyed and/or removed to at least 99.99%. Destruction and Removal Efficiency (DRE) is defined in Equation 1.

$$DRE = \frac{POHC_{in} - POHC_{out}}{POHC_{in}} \times 100\% \quad (1)$$

Trial burns are very costly to perform, with a considerable portion of the cost being sampling and analysis directed toward determination of DRE of the POHCs. Due to this high cost of determination, DRE is not a suitable quantity for frequent monitoring of incinerator performance.

Another shortcoming of DRE is that it does not address Products of Incomplete Combustion (PICs) from incinerators, but only the POHCs. It is possible that PICs could be produced, such as chlorinated dibenzodioxins, that can be more hazardous than their parent POHCs.

On-Line Performance Indicators

EPA's Air and Energy Engineering Research Laboratory (AEERL) in Research Triangle Park, NC, has been working to develop an on-line performance indicator for combustors burning hazardous waste. In particular, this on-line performance indicator must be easy to measure and inexpensive. Ideally, an on-line "PIC Monitor" would be useful, but, to date, on-line continuous measurement of trace organics has not progressed outside the laboratory. Therefore, due to current technology limitations, any on-line performance indicator must use only measurement techniques available today at a reasonable price. The new proposed RCRA regulations may require monitoring of CO and/or total hydrocarbons (THC) on a continuous basis in all combustors burning hazardous waste. It seems appropriate to use these analyzers as the starting point for an on-line performance indicator.

An additional rationale for developing a performance indicator would be to provide a uniform basis on which to compare emissions from incineration of different wastes at different combustion conditions to predictions from AEERL's mathematical waste release model^{1,2}.

A typical hazardous waste consists of many different compounds but, in terms of an ultimate analysis, any incinerable waste would contain C, H, N, O, ash, plus a host of other compounds, such as heavy metals, halogens, sulfur, and phosphorus. Since incineration is combustion, the preferred end products are CO₂ and water vapor. However, due to fluctuations in feed composition, Btu content, or batch charging, transients can occur that have the potential to significantly deviate from optimal combustion conditions³. In this case, PICs can be created, with the predominant PICs being CO, unburned volatile and semi-volatile hydrocarbons (possibly halogenated,

oxygenated, or nitrogenated), and soot, possibly containing condensed non-volatile organic material. Figure 1 illustrates these phenomena.

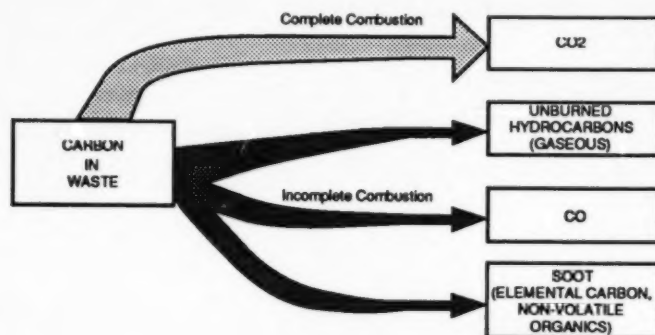


Figure 1. Fate of Waste Carbon

Not all PICs can be continuously measured, since trace organics can be present in exceedingly small quantities. CO and THC have been used as "surrogate" indicators of the presence or absence of significant quantities of PICs. Boiler operators have long used Combustion Efficiency (CE), defined in Equation 2, to monitor performance of boilers burning conventional fuels, such as fuel oil.

$$CE = \frac{CO_2 - CO}{CO_2} \times 100\% \quad (2)$$

CE has the advantage of being a simple calculation that gives a good indication of boiler performance, although it neglects other PICs formed during fuel combustion. When burning conventional fossil fuels, though, where transient excursions can be minimized by utilizing proper feeding techniques, CO is the predominant PIC, since the reaction described in Equation 3 is generally believed to be the final step in the complex mechanism of combustion.



However, when burning hazardous waste, alone or with conventional fuels, other PICs could be formed in significant quantities, lessening the usefulness of Equation 2.

In addition, the composition of the waste feed has a significant effect on which PICs are predominantly formed. Experiments performed in a 73 kW rotary kiln incinerator simulator burning a variety of pure liquid compounds bound on corn cob sorbent^{4,5} showed that different wastes produce different dominant PICs. For example, CO is predominantly measured when burning batches of CCl₄, partially due to the fact that Flame Ionization Detectors (FIDs) used in THC analyzers measure only C-H bonds. Toluene produced soot preferentially. AEERL has pursued the potential for expanding on the definition of CE to take into account the fate of all unburned carbon in the incinerator, so as to account for the effects of waste composition, especially POHCs, on PIC production.

Unsatisfied Oxygen Demand

By utilizing time-integrated responses from process gas analyzers rather than instantaneous or averaged responses, it is possible to derive an indicator of the relative degree of local oxygen starvation that waste material was exposed to while passing through the incinerator. This new performance indicator, dubbed Unsatisfied Oxygen Demand (UOD), is a quantity that uses CO, THC, and soot to calculate UOD based on the carbon content of the initial feed and the estimated carbon content of the surrogate PIC species, then weighting these components according to their stoichiometric oxygen requirements. At this point in time, UOD is a "Straw Man" quantity that is being proposed as a starting point for examination of incinerator performance. Tests have been performed examining only transient puffs, or plugs of unburned material produced due to rapid waste evolution and oxygen starvation resulting from batch feeding, in a rotary kiln incinerator simulator, and UOD has been primarily developed as a uniform puff indicator with which to examine puff magnitudes resulting from batch charging of different wastes. There are no indicators of what constitutes an acceptable UOD and, at this point, UOD does not take into account unburned material in the incinerator residues. However, UOD does attempt to provide a parameter that couples the responses of the three predominant surrogate PIC components (CO, THC, and soot) to the combustion conditions in the incinerator.

If the THC and CO concentrations leaving the incinerator, prior to any downstream flue gas cleaning equipment, are integrated with respect to time, then the resulting quantities, I_{thc} and I_{co} , shown in Equations 4 and 5, represent the total emissions of THC and CO over the time measured. Any transients that occurred in the incinerator during the monitoring time would be contained within these quantities. This is different than the current practice of using instantaneous or averaged responses from gas analyzers.

$$I_{thc} = \int_0^{\tau} THC \, dt \quad (4)$$

$$I_{co} = \int_0^{\tau} CO \, dt \quad (5)$$

In the above equations, τ is the elapsed time during the integration process.

In order to convert the above integrated numbers, which are typically expressed in units of ppm-seconds, into useful quantities, the total stack gas flow rate and the molecular mass of the two surrogate species must be taken into account, assuming ideal gases. Since THC results are generally expressed in ppm-methane equivalents, the molecular mass of methane, 16, will be used. Therefore,

$$m_{thc} = \frac{16 I_{thc} PV}{RT} \quad (6)$$

$$m_{co} = \frac{28 I_{co} PV}{RT} \quad (7)$$

In the case of particulate matter, a distinction must be made between the carbonaceous and non-carbonaceous fractions of the flyash. To do this, a sample must be taken of the flyash, which must then be analyzed for carbon content. Unfortunately, no "soot monitors" are available to give continuous

measurements of flyash carbon content so a conventional carbon analysis of the flyash must be used to give the carbon content. The carbon analysis is very inexpensive and rapid when compared to a GC/MS analysis directed at residual POHC measurements to determine DRE.

The particulate sample is collected on the filter contained in the THC analyzer. AEERL uses Beckman 402 heated hydrocarbon analyzers for THC measurements. These analyzers have a filter housing where a small quartz filter can be installed prior to sampling. This filter can be weighed before and after the sample time, and the mass of particulate matter on the filter can be determined. The collected particulate contains all matter in the gaseous sample that is not volatile at the temperature of the filter housing, which is 150 °C (300 °F), which includes semi-volatile and non-volatile organics, soot, and inorganic material normally associated with flyash. Volatile compounds penetrate the filter and are detected by the FID.

To estimate particulate concentrations in the stack gases, it is necessary to know the volumetric flow rate of sample gas into the THC analyzers (V_s). Neglecting any variations due to non-isokinetic sampling,

$$m_p = m_{\text{sample}} \frac{V}{V_s} \quad (8)$$

where m_{sample} is the mass of particulate captured on the filter.

Using the three quantities of m_{thc} , m_{co} , and m_p , along with the weight percent of carbon in each fraction, x_{thc} , x_{co} , and x_p , the mass of waste fed during time τ , m_{waste} , and mass percent carbon in the waste, x_{waste} , Equation 9 can be used to calculate CP (Carbon Penetration), the fraction of feed carbon leaving the combustor as partially oxidized or unoxidized carbonaceous material.

$$\text{CP} = \frac{x_{\text{thc}}m_{\text{thc}} + x_{\text{co}}m_{\text{co}} + x_p m_p}{x_{\text{waste}}m_{\text{waste}}} \quad (9)$$

The three PIC fractions each force different oxygen demands on the incinerator. For example, CO is a partially oxidized species, and requires less oxygen to become completely oxidized than, say methane. To take this into account, each of the factors in CP can be weighted according to the stoichiometric oxygen required to completely burn each component. This weighting factor, w_i , when applied to each term in Equation 9, results in UOD, the Unsatisfied Oxygen Demand due to unburned carbon, as shown in Equation 10.

$$\text{UOD} = \frac{x_{\text{thc}}m_{\text{thc}}w_{\text{thc}} + x_{\text{co}}m_{\text{co}}w_{\text{co}} + x_p m_p w_p}{x_{\text{waste}}m_{\text{waste}} w_{\text{waste}}} \quad (10)$$

The UOD quantity reflects the relative requirements for oxygen of the measured PIC components. It reduces the contribution of partially oxidized species such as CO, and increases the contribution of unoxidized species such as organics and soot. It also provides a common basis for measurements of emissions of different types of waste.

Experimental Methods

Apparatus

The EPA rotary kiln incinerator simulator has been described in detail previously ^{4,5}. It has been established that the 73 kW (250,000 Btu/hr) pilot-scale simulator with a 58.4 kW (200,000 Btu/hr) afterburner/control temperature tower exhibits the salient features of full-scale units with thermal ratings 20 to 40 times larger. The simulator matches the volumetric heat release, gas-phase residence time, and temperature profile of many full-scale units, and yet is flexible enough to allow parametric testing. Figure 2 is a schematic drawing of the simulator.

Batch charges are introduced through a sliding gate/ram assembly downstream of the continuous natural-gas-fired oxygen-enriched burner.

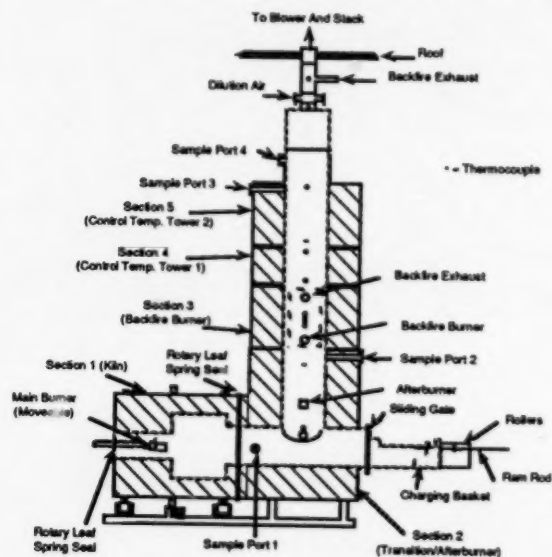


Figure 2. EPA Rotary Kiln Incinerator Simulator

Quantification of emissions requires the real-time measurement of system response variables. These dependent variables include peak responses of O_2 , CO , CO_2 , NO_x , and total volatile hydrocarbon (THC) concentrations measured by continuous flame ionization detection (FID) and reported in equivalent parts per million methane. HCl is not measured continuously at this time, but will be taken into account in the future. At present, HCl is considered negligible on soot. Duplicate sets of these Continuous Emission Monitors (CEMs) were placed at sample ports 1 and 4. Volatile organics are defined as those in the gas phase at 420 K (300°F), the temperature of the heated sample line. In addition to the measurement of the continuous concentrations of the gaseous species, time integration of the CO and THC were done in real time by a microcomputer-based data acquisition system.

Particulate matter was measured by placing tared quartz filters into the heated filter housing in the THC analyzer. Weight differences were calculated after the sampling time had elapsed.

Parametric Testing

In the majority of these experiments, charges to the kiln consisted of 250 g (0.55 lb) quantities of polyethylene pipe cut into 15.24 cm (6 in) pieces. The charges were fed into the rotary kiln incinerator simulator at approximately 10 minute intervals. After a given charge was completely burned away, filters were weighed, new, tared filters were installed, and the integration counters were reset in preparation for the next charge.

In addition to the tests with polyethylene, experiments were performed using two other surrogate liquid wastes: toluene and carbon tetrachloride. Experimental procedures were identical for the liquid tests, except that for liquids, 100 g (0.22 lb) of liquid was added onto 180 g (0.4 lb) of corncob sorbent in a 0.95 liter (1 qt) cardboard container prior to feeding.

For these experiments, the rotary kiln conditions were held constant to the values shown in Table 1. The secondary combustion chamber (SCC) was operated at a variety of different conditions, varying the SCC temperature, oxygen partial pressure (P_{O_2}), and residence time, as shown in Table 2. All of the response variables were measured, and the quantities defined in Equations 9 and 10 were calculated. For the liquid experiments, conditions in the secondary combustion chamber were held at the baseline conditions listed as Run Designation 1, with the afterburner not operating.

Table 1. Rotary Kiln Incinerator Simulator Operating Conditions

Firing Rate	58.4 kW (200,000 Btu/hr)
Temperature	850 °C (1560 °F)
Rotation Speed	0.5 rpm
Primary Burner Stoichiometry (based on air/fuel ratio)	2.0

Table 2. Secondary Combustion Chamber Conditions

Run Designation	SCC T, °C	P_{O_2} , kPa	Res. Time, s
1	707 (1305 °F)	13.27 (0.131 atm)	5.19
2	865 (1590 °F)	12.26 (0.121 atm)	3.40
3	656 (1212 °F)	14.08 (0.139 atm)	5.08
4	943 (1729 °F)	11.55 (0.114 atm)	3.18
5	977 (1791 °F)	10.03 (0.099 atm)	3.44
6	885 (1626 °F)	11.04 (0.109 atm)	3.71
7	756 (1392 °F)	14.49 (0.143 atm)	4.55
8	776 (1429 °F)	13.57 (0.134 atm)	4.93
9	941 (1725 °F)	13.78 (0.136 atm)	3.39

Results

Figure 3 shows the contributions of hydrocarbons, CO, and soot to the gas phase carbonaceous material for nine afterburner conditions. CO and soot are the primary components, and hydrocarbons make up only a small fraction of the total gas phase carbon. However, when displayed in terms of UOD, CO's contribution is lessened and the contribution of THC to the total gas phase oxygen deprivation is increased. This phenomenon is shown in Figure 4. Especially interesting are the differences in relative contributions of the

different species at different combustion conditions. In certain cases, THC was a significant fraction of the total emissions; in others it is almost negligible, at least on the basis of stoichiometric requirement in the gas phase. Another noticeable phenomenon is the relative insensitivity of the amount of soot formed to the combustion conditions. A possible explanation of this phenomenon is that the reduction is mostly attributable to pyrolysis of non-volatile organic material and its subsequent combustion. Although soot can oxidize, the pyrolytic conditions present within the puff appear to present a situation where diffusion of oxygen into the fuel rich zones is a rate controlling step. The soot particles probably don't see sufficient oxygen to burn, since any products of pyrolysis would react with the available oxygen as they diffused away from the soot particles.

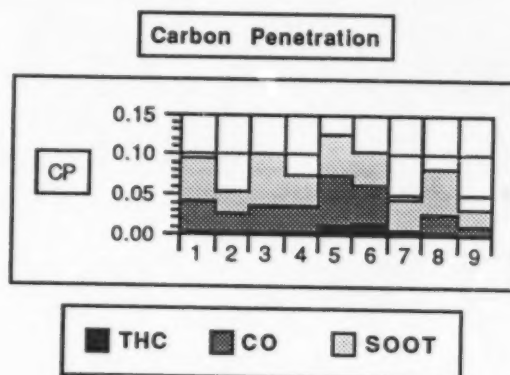


Figure 3. Carbon Penetration Values for Polyethylene Tests

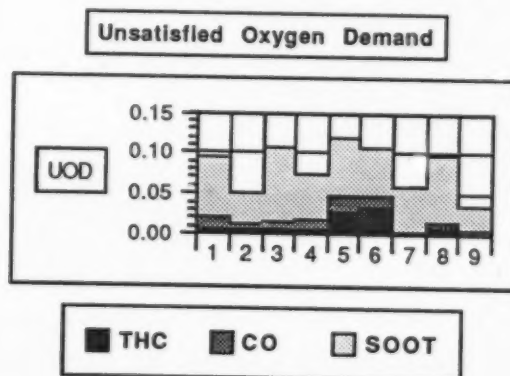


Figure 4. UOD Values for Polyethylene Tests

In addition, when data from different feed materials are compared, the differences in the relative contributions of the three components are readily apparent. As Figures 5 and 6 illustrate, not only are the absolute values of UOD different for the different wastes at the same combustion conditions, but also the relative fractions of the PIC components were different at the same combustion conditions. CCl_4 is not included in these plots because the inaccuracies of the filter weight measurements indicated a much larger contribution of soot than was really there; the particulate mass measurements were all of the same order of magnitude as the precision of the analytical balance that was used.

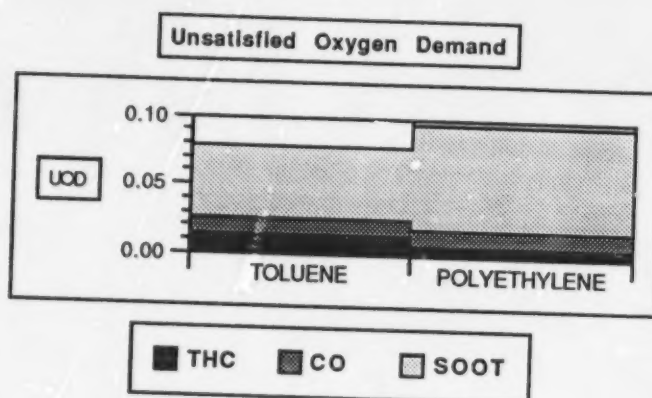


Figure 5. Comparison of UOD for Polyethylene and Toluene

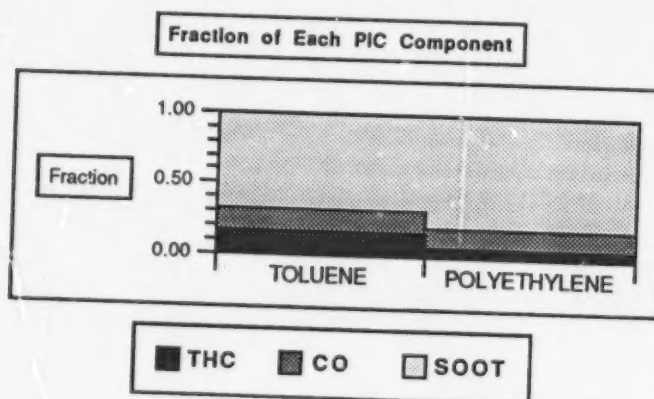


Figure 6. Relative Fractions of PIC Components

The results from this study indicate that utilizing UOD as the primary parameter describing "puff magnitude" provides a uniform basis with which to compare the behavior of different waste streams at different combustion conditions when incinerated in a batch mode. UOD provides a simple method to calculate the propensity of a given waste to "puff" when fed in a batch mode, yet takes into account all of the easily measurable PICs that are created during short term transients.

Conclusions

It is possible to use easily measured continuous or semi-continuous incinerator performance indicators to derive a uniform puff indicator to characterize incinerator failure modes caused by batch feeding techniques. This uniform indicator, UOD, can be calculated for a variety of waste materials, and takes into account unburned hydrocarbons, CO, and soot. In addition, UOD takes into account the variations in emissions from different waste streams, and provides a starting point for ranking different waste streams according to their propensity to form puffs.

This indicator is meant only as a starting point from which to examine incinerator, boiler, and furnace emissions. The relationship between this

indicator and incinerator operating parameters is not yet established. The goal of proposing this performance indicator is to provide a uniform indicator of incinerator performance at a variety of combustion conditions and feed materials.

To date, all work in this area has been concentrating on transients produced by batch incineration of small amounts of surrogate wastes, either solids (plastics) or containerized liquids bound on sorbents. Future work will include examining the applicability of this concept to steady-state incineration of hazardous wastes and co-firing of hazardous wastes with conventional fuels in boilers and furnaces.

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Nomenclature

CP	Carbon Penetration (dimensionless)
I_{CO}	integral of CO trace with respect to time (ppm-s)
I_{THC}	integral of THC trace with respect to time (ppm-s)
m_{CO}	total mass emissions of CO during time τ (lb)
m_p	total mass emissions of particulate matter during time τ (lb)
m_{THC}	total mass emissions of THC during time τ (lb)
m_{waste}	total mass of waste fed during time τ (lb)
P	total system pressure (atm)
R	ideal gas constant ($ft^3 \cdot atm / lbmol \cdot ^\circ R$)
T	temperature at standard conditions ($^\circ R$)
UOD	unsatisfied oxygen demand (dimensionless)
V	volumetric flow rate of stack gas at standard conditions (ft^3/s)
V_s	volumetric sampling rate of THC analyzer (ft^3/s)
w_{CO}	stoichiometric requirement to burn CO (dimensionless)
w_p	stoichiometric requirement to burn soot (dimensionless)
w_{THC}	stoichiometric requirement to burn hydrocarbons (dimensionless)
w_{waste}	stoichiometric requirement to burn waste (dimensionless)
x_{CO}	mass fraction of carbon in CO (dimensionless)
x_p	mass fraction of carbon in soot (dimensionless)

x_{thc} mass fraction of carbon in hydrocarbons (dimensionless)

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